COPPER DOPED TITANIUM DIOXIDE (TiO_2) NANOPARTICLES FOR ENHANCED PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT IRRADIATION

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ABSTRACT

Titanium dioxide (TiO_2) is best known for its inexpensiveness and highly available as a photocatalyst. However, due to its wide-bandgap of 3.2 eV and the fast recombination of electron-hole pair, they have contributed to the inability to use the sunlight sufficiently as well as hindering for any reaction to happen. The objectives of the title are to synthesize a copper (Cu) doped TiO_2, to inspect the photocatalytic activity of the synthesized TiO_2 and to study the kinetic of the degradation of methylene blue (MB). A Cu salt is first synthesized using copper nitrate ($Cu(NO_3)$) mixed in the glycerol phase. The preparation of TiO_2 was carried out by the sol-gel method and the resulted Cu salt is added into it to in a 10 wt.% Cu/TiO_2 manner. The resulted gel was aged for a day before it was heated up in the oven for 24 hours, which resulted in powder form. It was grinded and calcinated at 300 ^oC for an hour. The photocatalytic activity of the synthesized catalyst was inspected with the degradation of methylene blue (MB). As a result, the photocatalytic activity had been increased and the $K0\ (\left(\frac{k0H}{K0}\right) + k0$ is 0.03236 mg L^{-1} min^{-1} while K_0 is 9.32615 X $10^{-3\ 4}$L mg^{-1}.

diujikan dengan degradasi MB. Photoaktiviti katalis telah ditingkatkan akibatnya dan $K0$ ($\left(\frac{k0H}{K0}\right) + k0$ yang didapati ialan 0.03236 mg L^{-1} min^{-1} dan K_0 ialah 9.32615 X 10^{-3} ^{4}L mg^{-1}.

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LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infra-Red
UV-Vis	Ultraviolet/Visible
MB	Methylene Blue
C	Concentration
C_0	Initial Concentration
C_{01}	Initial Concentration of 70 ppm MB
C_{02}	Initial Concentration of 50 ppm MB
C_{03}	Initial Concentration of 30 ppm MB
C/C_0	Ratio of Current Concentration to the Respect of the Initial Concentration
C/C_{01}	Ratio of Current Concentration to the Respect of the Initial Concentration of 70 ppm MB
C/C_{02}	Ratio of Current Concentration to the Respect of the Initial Concentration of 50 ppm MB
C/C_{03}	Ratio of Current Concentration to the Respect of the Initial Concentration of 30 ppm MB
T	Temperature

1 INTRODUCTION

1.1 Motivation and statement of problem

Photocatalyst is a light-activated catalyst. When a photocatalyst is exposed to light, it absorbs photon energy and causes various chemical reactions. Metal complexes and semiconductor catalyst are recognised as photocatalyst materials (Kameyama et al, 2010). Titanium dioxide is possibly one of the best photocatalyst. This is because of its high efficiency, inexpensiveness, easy production, photochemical and biological stability, and inert to the environment and human beings (Paola et al, 2008; Bendavid et al, 1999; Ku et al, 1996). Due to these several reasons, a lot of researches were done in the development of photocatalyst as a result, it had being applied in many different fields, such as degradation of organic pollutants in water and wastewater (Wen et al, 2006; Liu et al, 2010; Yousef et al, 2011, Guo et al, 2012), as a disinfectants (Shieh et al, 2006; Chang et al, 2011), and for air-cleaning purpose (Sano et al, 2012; Dong et al, 2013).

Despite the advantages of using titanium dioxide as a photocatalyst, a major problem faced in using TiO_2 photocatalyst is its wide-bandgap of having a value of 3.2 eV (Jiang et al, 2010; Liu et al, 2011; Dong et al, 2013). The sunlight consists of only a small fraction, approximately 3-5% (Kim et al, 2012; Zou et al, 2001; Maeda et al, 2006) of ultraviolet (UV)- light, 45% of visible light (Dong et al, 2012) while the rest is infrared light. In other words, its wide-bandgap has contributed to the inability to use the sunlight sufficiently, as the 3.2 eV bandgap of TiO_2 can only be activated under the near and UV-light only. Quite simply, the rest of the light which has lower energy (wider wavelength) than UV-light is not suitable for the semiconductor electronic band gap cannot generate electron-hole pairs and

is therefore wasted as heat (Jiang et al, 2010). Another problem faced when using titanium dioxide is the fast recombination of electron-hole pair (Mills, 1997), thus hindering for any reaction to take place.

1.2 Objectives

The following are the objectives of this research:

- To synthesize the copper doped titanium dioxide.
- To inspect the photocatalytic activity of the copper doped titanium dioxide.
- To study the kinetic of the photocatalytic reaction.

1.3 Scope of this research

The following are the scope of this research:

i) Synthesizing of copper doped TiO_2 through sol-gel method.

ii) Characterization to be done with Fourier-Transform infrared spectra (FTIR).

iii) Photocatalytic test with the degradation of methylene blue (MB).

iv) Kinetic studies of the degradation of methylene blue (MB).

1.4 Main contribution of this work

The following are the contributions

- The degree of increased in the photocatalytic activity through the research will not only bring a better understanding in photocatalyst, but it will serve as a reference to the other researchers to come up with a better idea to further develop better photocatalyst in the future. This will ultimately reduce the bandgap of the titanium dioxide as well as the rate of recombination of electron-hole pair.
- This would lead the world of using photocatalyst which only utilise the sunlight for any specific reaction to happen, without the

consideration like the conventional catalyst which requires certain reaction temperature and pressure.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the fundamental of mechanism of the photocatalyst, followed by the doping of metals, how doping would helped in increasing the photocatalytic activity, and the kinetic studies.

Chapter 3 gives an insight of how the synthesized Cu salt is made before being doped into TiO_2 to create the novel synthesized Cu doped TiO_2, along with the materials and the equipments used during the research and for the kinetic studies.

Chapter 4 is gives a review of the comparison of TiO_2 and the synthesized Cu doped TiO_2. The photocatalytic test data is analysed with the aid of the graph plots. The kinetic studies is discussed here as well.

Chapter 6 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Overview

The activation of the semiconductor to take part in a reactor is first being explained through the excitation of the electrons from the electron valence through the bandgap and to the conduction band after absorbing a sufficient or more amount of energy from the sunlight. The two main obstructions faced in the photocatalytic reaction are the wide bandgap and the fast recombination of the electron-hole pair. Doping has so far been reported to be one of the way to curb such happenings by narrowing the bandgap to allow lower energy to be absorbed by the semiconductor for the excitation of electrons to happen. A kinetic studies of the photocatalytic activity is later discussed as well.

2.2 Introduction

For this chapter, it covers about the fundamental mechanism of the photocatalyst in semiconductor, specifically to titanium dioxide (TiO_2), later followed by the doping and how doping will affect the bandgap of TiO_2, which leads to the increase of photocatalytic activity. Kinetic study of the degradation of the methylene blue (MB) is discussed at the later part of the chapter.

2.3 Fundamental Mechanism of Photocatalyst

The fundamental mechanism of photocatalyst is the ability of a semiconductor to absorb photons creating reactive electron-hole pairs which

are capable of oxidizing most organic and inorganic compounds (Bloh et al, 2012). Often, a semiconductor is chosen for such particular reason due to its nature of having band gap, which separates both the valence band and the conduction band. Given enough energy in the form of photon provided by the light, absorbed by the semiconductor, for this case, TiO_2, the electrons in the valence band should achieve excitation state to excite from the valence band to the conduction band of the semiconductor. The energy of the photon can be calculated with the following formula:

$$E = hf$$

where E is the energy of the particle of light, called photon, h is the Planck constant of having a value of 6.63×10^{-34} Js, and f is the frequency of its associated electromagnetic wave. Simultaneously, a positively charged hole is created in the valence band. Varying reactions will take place with the surfaced adsorbed molecules (Mills et al, 1997), with the aid of these excited electrons that appear on the surface of the semiconductor in the conduction band.

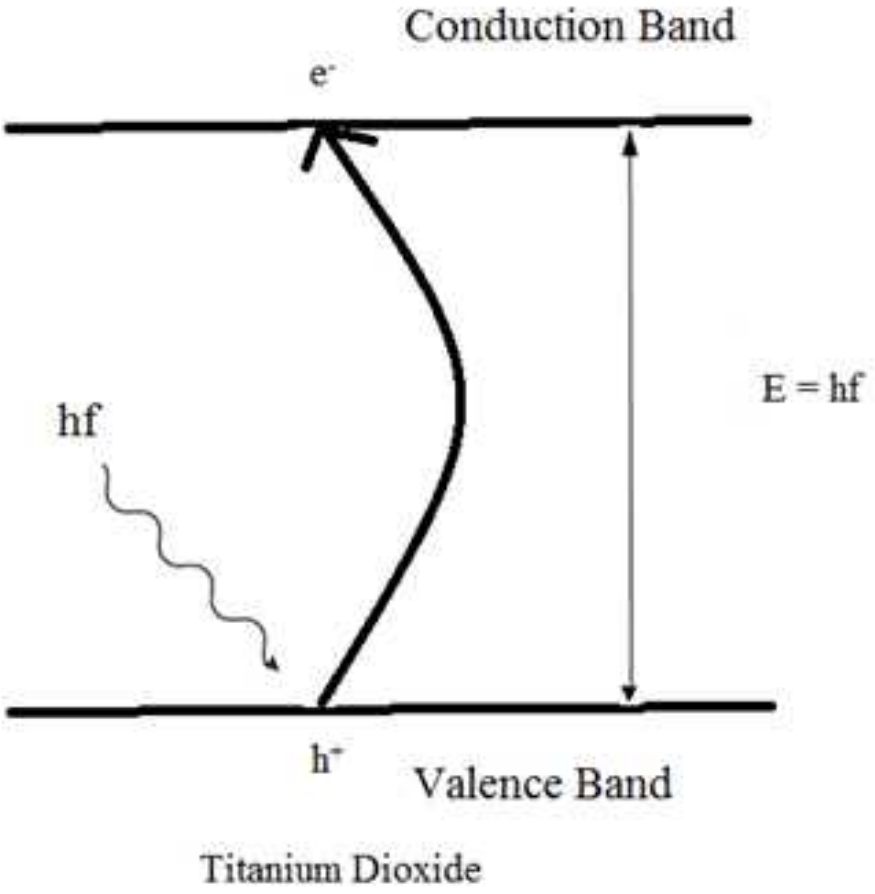

Figure 2.1: Fundamental mechanism of photocatalyst- Excitation of electron from the valence band to the conduction band.

The excited electrons in the conduction band which are responsible to carry out a reaction. Another point which is worth noticing is that due to the nature of bandgap, the photo-generated electrons in the bottom of the conduction band can have the sufficient negative redox potential to drive any reaction of lesser negative redox potential (Jiang et al, 2012). The reduction of carbon dioxide (CO_2) is one of the application that uses this feature of TiO_2 to carry out the experiment. Here, the researcher has briefly explained about how the excitement of electrons from the valence band after

absorbing sufficient energy from the sunlight to conduction band and to be involve in the reaction.

2.4 Doping

On the contrary, it is also due to the large bandgap of TiO_2 features, the utilization of the sunlight is very low. Which is also why doping is introduced to photocatalyst. Asahi et al (2001) first doped nitrogen into the TiO_2 which resulted in the increase of photocatalytic activity in the degradation of methylene blue (MB). They concluded that substitutional N doping causes bandgap narrowing through N 2p orbitals mixing with O 2p orbitals and their synthesized photocatalyst had shown to be activated under wavelength of 500 nm, which is in the visible light region. Ihara et al (2002) further explained that oxygen-deficient sites formed in grain boundaries are important to emerge vis-activity, and nitrogen doped in the part of oxygen-deficient sites are important as a blocker for reoxidation This is suggesting that the synthesized photocatalyst is using a great portion of the sunlight to carry out the reaction while having the sufficient negative redox potential to carry out the degradation of MB despite the bandgap being narrowed. Hence, at here, the researcher of the proposed study wants to point out that, the development of the photocatalyst is not all about being photosensitive to bring the TiO_2 to the visible light region yet to have sufficient energy to be photoexcited of an appropriate bandgap to carry out a certain specific reaction. This will lead to a vast developing of varied photocatalyst.

After the success of doping nitrogen to the TiO_2, a lot of doping had been done throughout the world, ranging from non-metal, for example, sulphur (Liu et al, 2007), carbon (Wang et al, 2007), silica (Periyat et al, 2008), to metal, such as ferum (Tieng et al, 2011), vanadium (Li et al,

2010), lanthanum (Wen et al, 2003), copper (Yoong et al, 2009), platinum, gold, and silver were reported as well by Peng et al (2012). To further increase the effectiveness of the doping, co-doping had been introduced which served as a promising approach (Liu et al, 2008). Co-doping, like nitrogen and sulphur (Wei et al, 2007), bismuth and boron (Bagwasi et al, 2013), sulphur and iron (Niu et al, 2013), carbon and iron (Wu et al, 2010). There are certainly a lot more of the experiments regarding doping on TiO_2 to list on. All of the researches give a significant bandgap narrowing as well as being photosensitive.

Among all, however, what catches the attention of the researcher is the copper doping. Copper is one of the metal, which does not go under oxidation easily (Wu et al, 2008). Of course, the fact of using noble metals is taken as consideration by the researcher, however, considering how expensive of those noble metals, therefore copper is taken as a choice as dopant.

2.5 Kinetic Studies of Methylene Blue (MB) Degradation

Here the reaction modeling of the MB degradation modeling will be reviewed. The modeling is done as to characterize the reaction itself with an equation so that the reaction can be predictable under various operating condition. This modeling is important also as to provide the design equation to design the photocatalytic reactor, where the equation on the rate of reaction is needed in order to design the volume of the continuous reactor or the reaction time as for the batch reactor.

In 2013, a model has been proposed by Sannino et al (2013) to model a reaction considering the concentration of the MB at that time, the

intensity of the light and the weight of the catalyst used. Hence a MB mass balance has been written as follows:

$$V \cdot \frac{dC(t)}{dt} = r(C, I) \cdot W_{TD}$$

Here the V is the solution volume (L). C(t) is the MB concentration (mgL^{-1}). *r* is the reaction rate ($gL^{-1}min^{-1}$). W_{TD} is the catalyst amount (g). And I is the light intensity reaching the catalyst surface ($mWcm^{-2}$).

Later on, the mass balance is further modelling the methylene blue concentration and the intensity of the light with the Langmuir-Hinshelwood mechanism rate law. Then, the Lambert-Beer law is used to further models the intensity of the light in the form Langmuir-Hinshelwood mechanism rate law to consider the screening effect, where the penetration of light decreases when the catalyst loading is increasing. Hence, the rate of degradation of MB is written as follows:

$$V \cdot \frac{dC(t)}{dt} = -K_1 \cdot \frac{b \cdot C(t)}{1 + b \cdot C(t)} \cdot \frac{\alpha \cdot I_0 \cdot e^{-k_1 \cdot [TiO_2]}}{1 + \alpha \cdot I_0 \cdot e^{-k_1 \cdot [TiO_2]}} \cdot W_{TD}$$

Where:

K_1 = Kinetic constant ($mg\ g^{-1}min^{-1}$)

α = Light absorption coefficient ($cm^2(mW)^{-1}$)

k_1 = Specific extinction coefficient per unit catalyst mass ($L\ mg^{-1}$)

I_0 = Light intensity incident on the reactor surface ($mW\ cm^{-2}$)

$[TiO_2]$ = Catalyst dosage ($mg\ L^{-1}$)

b = Adsorption coefficient ($L\ mg^{-1}$)

Still several weaknesses have been detected within this model. As mentioned before, the intensity of the light here has been modelled referring

to Langmuir-Hinshelwood mechanism rate law. As known, this Langmuir-Hinshelwood mechanism rate law is usually used to describe the reaction pathway of a catalytic reaction, where the reaction between two atoms is occurred when they are adsorbed on the surface of the catalyst as depicted as follows:

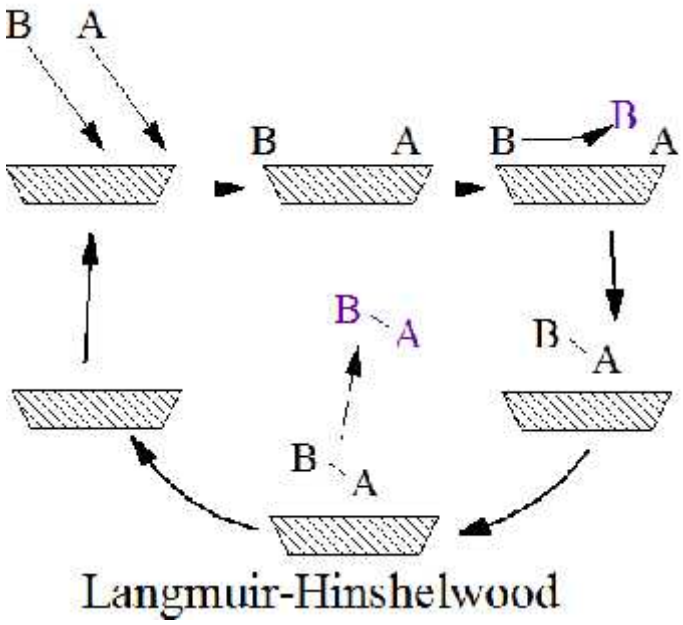

Figure 0.1: The reaction pathway of atoms as described by Langmuir-Hinshelwood mechanism rate law.

Hence, the doubt is raised when a rate law that characterize a reaction is used to model the effect of intensity of the light towards the degradation of the MB itself. Concrete evidence showing the incompatibility of the light intensity model is shown when we recalculate back the constant considering the light intensity using the value provided by Sannio et al (2013) as shown below that is used to model their degradation for catalyst weight 0.3 g and light intensity 32 $mWcm^{-1}$ in 100ml solution:

$\alpha = 0.000925\ cm^2\ (mW)^{-1}$

I_0 = 32 mWcm^{-1}

k_1 = 0.012 Lmg^{-1}

[TiO_2] = catalyst weight/ solution volume = 0.3 g/ 100 ml = 3000 mg/L

$$\frac{\alpha \times I_0 \times e^{-k_1 \times [TiO_2]}}{1+\alpha \times I_0 \times e^{-k_1 \times [TiO_2]}} = \frac{0.0 \quad \times 3 \times e^{-0.0 \quad \times 3}}{1+0.0 \quad \times 3 \times e^{-0.0 \quad \times 3}} = 6.87 \times 10^{-1} \; C$$

This value suggested that after considering the light intensity factor for the degradation of MB itself, the rate of degradation MB is actually ranging around value of 10^{-18} cm, which is not in parallel with Sannio et al (2013) data. For the MB degradation with 0.3 g catalyst and light intensity 32 mWcm^{-1}, the data of MB concentration vs time is analysed and the graph of rate of MB degradation vs concentration of MB is generated using Origin software as shown in figure 2.3.

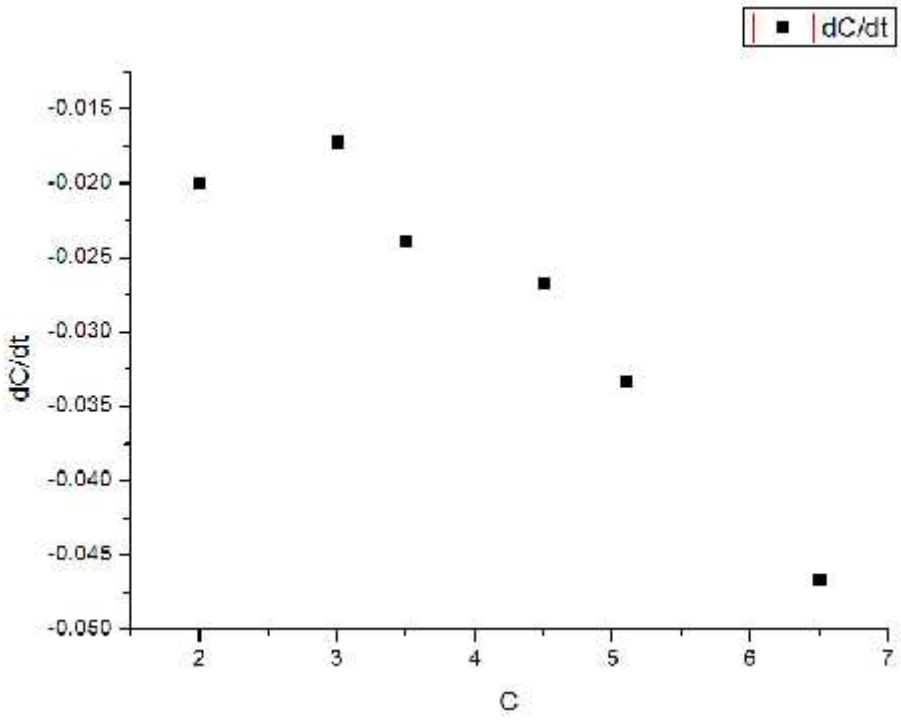

Figure 0.2: Graph of rate of MB degradation vs concentration of MB from Sannio et al (2013) data

As can be seen from the graph, the values of the rate of degradation are ranging around 0.075 $mgL^{-1}min^{-1}$ to 0.0475 $mgL^{-1}min^{-1}$. Looking back at the model proposed, if we replacing the remaining available constant back in to model (K_1 = 0.46 mg g^{-1} min^{-1}; b = 0.82L mg^{-1}; V = 100 mL; W_{TD} = 0.3 g; C_T = 2 mg/L to 6.5 mg/L), the rate of degradation obtained will be ranging around 10^{-18}, which is greatly deviating from the experimental data itself. Hence in this research, another model of equation had been explored to characterize our degradation of our MB which shown in chapter 4 later.

2.6 Summary

After surveying the literatures, to the author's best knowledge, therefore, the author had decided to use doping as a matter of increasing the photocatalytic activity and a proposed model equation is made.

3 MATERIALS AND METHODS

3.1 Overview

The copper salt is first synthesized before being doped into the synthesized TiO_2 to obtain the copper doped TiO_2. Characterization of the synthesized photocatalyst is followed. Lastly, the photocatalytic activity test is carried out with the degradation of the methylene blue.

3.2 Introduction

This part of the chapter will discuss on the procedures, along with the equipments on how the research is going to be conducted. The experiment can be divided into five sections as the following:

a) Preparation of Copper (Cu) Salt
b) Synthesis of Copper (Cu) Salt
c) Catalyst Preparation
d) Catalyst Characterization
e) Kinetic Study

3.3 Materials and Equipment

The materials that are used in the experiment are as followed:

- Acetic Acid (Sigma Aldrich Company)
- Ethanol 99.8% (Sigma Aldrich Company)
- Deionized Water
- Hydrazine Hydrate 64.5% (Sigma Aldrich Company)
- Copper-n-butoxide (Sigma Aldrich Company)
- Copper Nitrate (Sigma Aldrich Company)

- Ascorbic Acid (Sigma Aldrich Company)
- Glycerol

The equipments that are used in the experiment are:

- Oven
- Glass Furnace
- Hot Magnetic Plat Stirrer
- UV-vis spectrophotometre
- Batch reactor
- Water Cooling System
- Black Box
- High Intensity Lamp
- Centrifuge

The minor apparatuses that are used during the experiment:

- 250 mL beaker
- Weighing board
- Thermometer
- 5 mL measuring cylinder
- 50 mL beaker
- Parafilm
- 100 mL beaker
- 100 mL measuring cylinder
- Crucible
- Weigh balancer

- Mortar
- Magnetic rod
- 50 mL Centrifuge tube

Before the experiment is carried out, all of the minor apparatuses (except for parafilm) are rinsed with weak nitrate acid and dried in the oven for an hour to prevent any contamination.

The programmes used to study the kinetic study are:

- OriginPro 8
- Microsoft Excel 2007

3.4 Preparation of Copper (Cu) Salt

Two mixtures will be made before they are being mixed to prepare the Cu salt, addressing both mixtures mixture A and mixture B respectively.

3.4.1 Preparation of Mixture A

1. 50 mL of glycerol is measured in a 250 mL beaker.

↓

2. 10 mg of $Cu(NO_3)$ is weighed in the weighing board and mixed with the glycerol under magnetic stirring.

↓

3. The mixture is heated up to 85 ^{o}C and stopped, and left to cool down to the surrounding temperature.

1. 10 mL of ethanol is measured using the 45 mL centrifuge tube.

↓

2. 6 mL of hydrazine is measured using pipette and mixed with ethanol.

↓

3. The mixture B is shook vigorously and the colour of the mixture will turn into light brown.

3.4.3 Synthesis of Cu salt

1. 10 mL of mixture A is measured using a 50 mL beaker.

↓